ORGANOMETALLIC STRUCTURES - TRANSITION METALS
ANNUAL SURVEY COVERING THE YEAR 1972 (PART 2)*

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CONTENTS

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[*] Part 1: M.I. Bruce, J.Organometal.Chem., 53 (1973) 141.

ABBREVIATIONS

acac	acetylacetonate
azbH	azobenzene
bipy	2,2'-bipyridyl
COD	1,5-cyclooctadiene
Cy	cyclohexyl
DAB	2,3-diazabicyclo[2.2.1]heptane
dppe	1,2-bis(diphenylphosphino)ethane
DQ	duroquinone
$f_4$asp	1-(dimethylarsino)-2-(diphenylphosphino)tetrafluorocyclobutene
$f_4$fars	1,2-bis(dimethylarsino)tetrafluorocyclobutene
MA	maleic anhydride
py	pyridine
TCNE	tetracyanoethylene
terpy	2,2',2''-terpyridyl
THF	tetrahydrofuran
tol	tolyl

ms-TPP	meso-tetraphenylporphin
triphos	$CH_3C(CH_2PPh_2)_3$

GENERAL AND REVIEWS

As a result of the now extensive structural studies on many different types of organometallic complexes, several detailed treatments of the bonding of ligands to metals have appeared. Thus Russian workers have described[1] the electronic structure of the $Re(CO)_5$ group, and a bonding model for bent bis(π-cyclopentadienyl)metal complexes has been advanced.[2] The latter is based in part on structural information of seven $(\pi\text{-}C_5H_5)_2MX_2$ compounds, containing d^0, d^1 or d^2 metals. The relative energies of the various possible modes of coordination of acetylene to metals are in "encouraging agreement" with X-ray diffraction results.[3]

The bonding within metal atom clusters has always excited interest, and recent studies by Wade[4] have indicated correlations between skeletal structures and numbers of skeletal bonding electrons, with cluster bonding orbitals resulting from interactions of three atomic orbitals from each cluster atom. Applications include cage boranes and hydrocarbon-metal π complexes, as well as to metal carbonyl clusters. Systematic correlations between metal-metal interactions and electronic structure and position in the periodic table have been found in M_2X_9 confacial bioctahedra, including $Fe_2(CO)_9$.[5]

Recent reviews which have come to the author's attention include King's survey[6] of transition metal cluster complexes, and the latest in the Russian periodical reports on structural chemistry, covering carbonyl π complexes with metal-metal bonds,[7] and recent studies on complexes containing ruthenium, rhodium, osmium and iridium.[8] The structures of several nickel complexes are illustrated in an article on automated X-ray diffraction as an analytical tool.[9]

METAL CARBONYLS AND RELATED COMPOUNDS

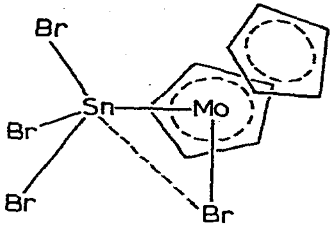
Reversible crystalline phase transitions have been found in $Mn_2(CO)_{10}$ (at 64-65°)[10] and in $Re_2(CO)_{10}$ (at 92°)[11], and ascribed to a change in configuration from staggered to eclipsed carbonyl groups.

In the thiocarbonyl $[Ir(CO)_2(CS)(PPh_3)_2]PF_6$, the Ir-CS bond length is shorter than Ir-CO, indicating both better σ donor and π acceptor properties for the CS ligand.[12] The phosphine ligands are at the apices of the trigonal bipyramidal cation.

COMPOUNDS CONTAINING METAL-METAL BONDS

(a) Transition metal-Main Group metal bonds. Structures of compounds containing Group IIB elements have been reported. In (terpy)$Cd[Mn(CO)_5]_2$, there is considerable distortion of the octahedral manganese coordination, the angles Cd-Mn-C(eq) falling in the ranges 86.5-90.0° and 76.2-79.7°. This effect may result from efficient packing of molecules.[13] The complex $Hg[Mn(CO)_5]_2$ contains linear two-coordinate mercury; the equatorial CO groups are bent towards this atom, and are approximately eclipsed.[14] Disorder among the CO and NO groups renders them indistinguishable in $Hg[Fe(CO)_2(NO)(PEt_3)]_2$; the three groups have the staggered configuration.[15]

In $(\pi-C_5H_5)_2Mo(SnBr_3)Br$ (1),[16] there is a fifth long (3.411Å) bonding interaction between the approximately tetrahedral $SnMoBr_3$ group and the fourth bomine atom, analogous to that found in (bipy)$(CO)_3ClMoSnMeCl_2$.[17] Both the cis and the trans isomers of $Ru(GeCl_3)_2(CO)_4$ contain octahedrally coordinated ruthenium.[18] The Ru-Ge bond lengths are the same, and chemically different Ru-C bonds have the same length in both isomers, and are consistent with an unusual π bonding ability for the $GeCl_3$ groups.



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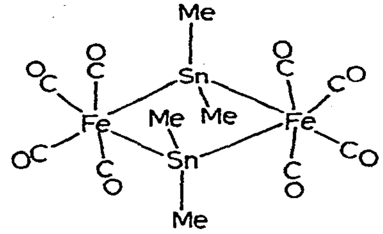

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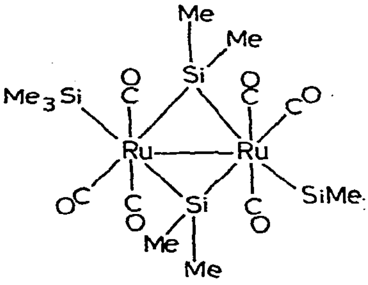
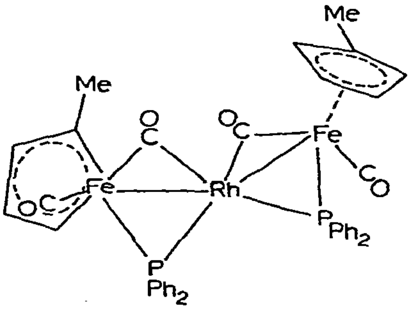


(3)

The structure of $[Me_2SnFe(CO)_4]_2$ (2) reveals the expected Sn_2Fe_2 ring,[19] and is similar to that of $[Et_2GeFe(CO)_4]_2$;[20] although the Sn-Fe bond length is close to the Sn^{IV}-Fe^{II} covalent radii sum, the Sn-Fe-Sn angle is 77°. Following the determination[21] of the structure of $[(Me_3Si)(CO)_3Ru(SiMe_2)]_2$ (3), which is similar to that of the tin analogue,[22] the metal-metal interaction in complexes of the type $L_6Ru_2Cl_3$ ($L = PR_3$, for example) has been reevaluated. An MO scheme is suggested, and accords with the observed presence or absence of metal-metal bonding in these complexes, as appropriate.

(b) Complexes containing only transition metals. An open, non-linear Fe-Rh-Fe sequence has been found in $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)\}_2]PF_6$ (4), the strongly basic PPh_2 groups resulting in the opening of the expected triangular cluster.[23]



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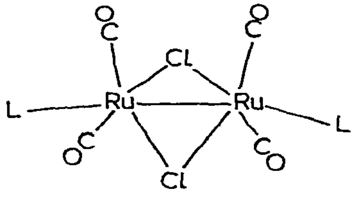
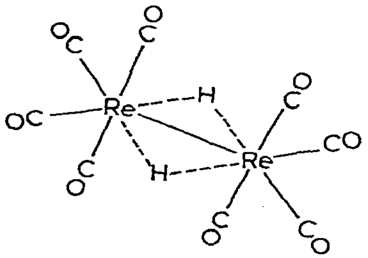


(5)

With bulky phosphines, carbonylated $RuCl_3$ solutions afford diamagnetic binuclear complexes $Ru_2Cl_2(CO)_4L_2$ (5).[24] For L = PBu^t_2(p-tol), the complex contains a non-planar $RuCl_2Ru$ bridge, with an RuRu bond distance (2.632Å) indicating a bent metal-metal bond.

The new carbonyl hydride $H_2Re_2(CO)_8$ has structure (6), in which the hydrogen atoms are thought to lie in the plane of the four CO groups indicated.[25] The short Re-Re bond distance is consistent with some degree of direct metal-metal interaction.

Two independent determinations[26,27] of the structure of the anion in $Ba_3[Co_2(CN)_{10}].13H_2O$ have been described, and consequently discussions concerning the nature of the cyanocobalt(II) system and particularly of the catalytically active dimeric anion can now be held on a firmer basis. Comparisons with the isoelectronic $Mn_2(CO)_{10}$ and $[Co_2(CNMe)_{10}]^{4+}$ species were made; unexpectedly, the axial Co-CN bond is 0.075Å longer than the equatorial bond. Only minor discrepancies are found in the two reports, although values for one of the cell parameters are significantly different. Axial Co-C and equatorial C-N bond lengths also differ significantly, although the sum is the same. The coordination geometry about the barium ion is described as an Archimedean antiprism[27] or as a trigonal dodecahedron,[26] although there are significant distortions from both limiting cases.



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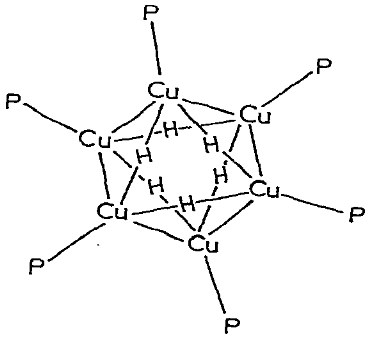
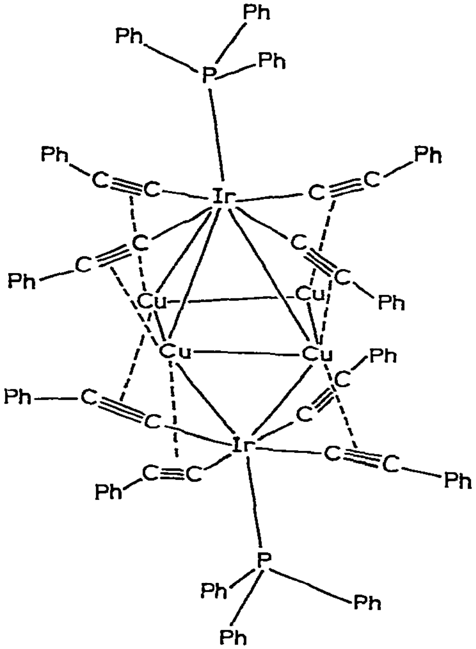


(7)

Further studies of Group IB cluster complexes have been reported. Full details of the structure determination of $H_6Cu_6(PPh_3)_6$ (7;$P = PPh_3$) are available,[28] the six hydride ligands probably being located along the six long Cu–Cu bonds, as shown. The related $[Au_6\{P(\underline{p}\text{-tol})_3\}_6]^{2+}$ cation has been described briefly.[29] The cluster is a distorted centrosymmetric octahedron. An extension of the cluster bonding ideas of Wade to both this, and the Au_{11} clusters described previously, is made. Full details of the structure of $Au_{11}I_3[P(C_6H_4F)_3]_7$ have appared.[30] Essentially the same metal atom cluster is found in this complex, in $[Au_{11}(PPh_3)_7]^{3+}$ [31] and $\{Au_{11}[P(C_6H_4Cl\text{-}\underline{p})_3]_7\}^{3+}$;[32] in the latter, thermal diffuse scattering was present, and the fluorophenylphosphine complex was fully refined instead.

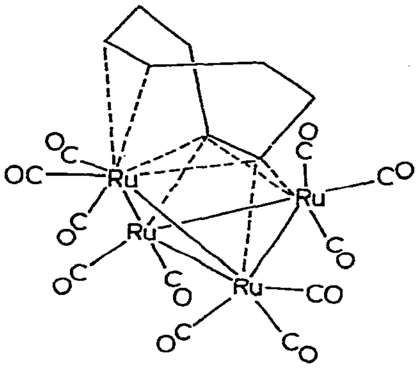
The author has found that reactions between Group IB acetylides and various organo-transition metal complexes are a fruitful source of a variety of interesting and novel complexes, including the unusual



(8)

hetero atom clusters exemplified by (8). In this complex,[33] the iridium and copper atoms have formal oxidation states of four and zero, respectively.

(c) Metal clusters containing hydrocarbon ligands. One product from the reaction between cycloocta-1,5-diene and $H_4Ru_4(CO)_{12}$ is (9), containing a cycloocta-1-en-5-yne ligand attached to an open Ru_4 cluster.[34] Full details of a similar complex, containing the cyclododecatrienyl ligand, are also available.[35] Preliminary details of the structure of $(Ph_2C_2)_2Os_3(CO)_9$ show the presence of a nearly equilateral triangular Os_3 cluster.[36]



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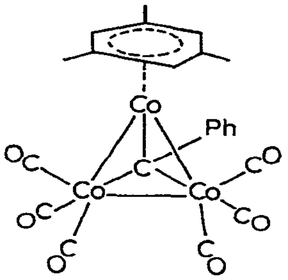

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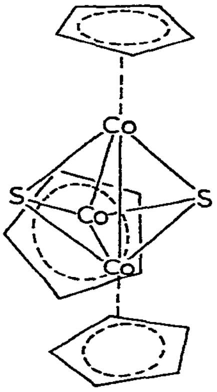

(11)

Interaction of mesitylene and $PhCCo_3(CO)_9$ affords (10), in which the arene is π-bonded to one of the three cobalt atoms.[37] Following studies of a number of trinuclear π-cyclopentadienylmetal clusters of cobalt and nickel, results of the structural determinations of $[(\pi\text{-}C_5H_5)Co]_3(CO)(S)$, $[(\pi\text{-}C_5H_5)Co]_3S_2$, and the monocation derived from the latter, $\{[(\pi\text{-}C_5H_5)Co]_3S_2\}^+$ (11), have been reported.[38] Variations in Co-Co bond distances are in accord with a bonding model which assumes no antibonding electrons in the carbonyl sulphide, one in the cationic disulphide, and two in the neutral disulphide.

(continued on p. 165)

TABLE <u>Metal-metal bond length determinations (1972)</u>

Bond	Length (Å)	Complex	Reference*
Cr-Cr	2.276(2)	$[(\pi\text{-}C_5Me_5)Cr(CO)_2]_2$	2-93
Mo-Sn	2.691(4)	$(\pi\text{-}C_5H_5)_2Mo(SnBr_3)Br$	2-16
W-Fe	2.81	$(\pi\text{-}C_5H_5)(CH{:}CHCOPh)FeW(CO)_6$	1-21
Mn-Cd	2.760, 2.799	$(terpy)Cd[Mn(CO)_5]_2$	2-13
Mn-Hg	2.610(2)	$Hg[Mn(CO)_5]_2$	2-14
Mn-Ge	2.43(1)	$Br_3GeMn(CO)_5$	1-7
Mn-Mn	2.90	$Mn_2(CO)_8(PMePh_2)_2$	2-127
	2.909(3)	$Mn_2(CO)_9C(OMe)Ph$	1-98
	2.94	$Mn_2(CO)_8(AsMe_2Ph)_2$	2-127
	3.012(2)	$Mn_2(CO)_8(C_4H_6)$	2-61
Re-Re	2.896(3)	$H_2Re_2(CO)_8$	2-25
	3.04	$Re_2(CO)_{10}$	1-4
	3.126(3)	$(\underline{ms}\text{-}TPP)[Re(CO)_3]_2$	2-118
Fe-Hg	2.534(2)	$Hg[Fe(CO)_2(NO)(PEt_3)]_2$	2-15
Fe-Ge	2.28(1)	$(\pi\text{-}C_5H_5)(\pi\text{-}C_4H_6)FeGeCl_2Me$	1-8
	2.438(4)	$[(\pi\text{-}C_5H_5)Co(CO)]_2(GeCl_2)_2Fe(CO)_4$	1-9
Fe-Sn	2.631(11)-2.647(8)	$[(Me_2Sn)Fe(CO)_4]_2$	2-19
Fe-Fe	2.39	$(Ph_3diazepin)Fe_2(CO)_6$	2-117
	2.467(2)-2.506(2)	$\{[(\pi\text{-}C_5H_5)Fe(CO)]_4\}^+$	2-20
	2.490(2)	$(DAB)Fe_2(CO)_6$	1-102
	2.506(1)-2.530(1)	$[(\pi\text{-}C_5H_5)Fe(CO)]_4$	1-19
	2.53	$(Ph_2pyridazine)Fe_2(CO)_5(PPh_3)$	1-103
	2.535(2)	$Fe_2(CO)_7C[2,6\text{-}(MeO)_2C_6H_3](OEt)$	2-113
	2.54	$[C(OMe){:}C(OMe)CH{:}C(CHPh_2)Fe(CO)_3]Fe(CO)_3$	2-82

	2.554	$(Ph_2PC\equiv CCF_3)Fe_2(CO)_5$		1-18
	2.596(4)	$(C_{12}H_8C=C=C=CC_{12}H_8)Fe_2(CO)_6$		2-79
	2.597(3)	$(Ph_2pyridazine\text{-}MA)Fe_2(CO)_6$		2-48
	2.679(6)	$(f_4asp)Fe_3(CO)_9$		2-132
	2.684(4)	$C_{16}H_{16}Fe_3(CO)_9$		1-68
	2.780	$Fe_2Pt(CO)_9(PPh_3)$		1-22
	2.863(6)	$(f_4asp)Fe_3(CO)_9$		2-132
Fe-Rh	2.660, 2.671(2)	$[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)\}_2]^+$		2-23
Fe-Pt	2.526	$Fe_2Pt(CO)_9(PPh_3)$	(trans to CO)	1-22
	2.550(5)	$FePt_2(CO)_5[P(OPh)_3]_3$	[Fe-Pt(CO)]	1-23
	2.583(6)	$FePt_2(CO)_5[P(OPh)_3]_3$	[Fe-Pt(P(OPh)$_3$)]	1-23
	2.605	$Fe_2Pt(CO)_9(PPh_3)$	(trans to PPh$_3$)	1-22
Ru-Hg	2.60-2.65	$2Ru(\pi\text{-}C_5H_5)_2\cdot 3HgCl_2$		1-81
	2.74	$Ru(\pi\text{-}C_5H_5)_2\cdot HgBr_2$		1-81
Ru-Si	2.391(7)-2.491(8)	$[Ru(SiMe_3)(SiMe_2)(CO)_3]_2$	(Ru-SiMe$_2$)	2-21
	2.507(8)	$[Ru(SiMe_3)(SiMe_2)(CO)_3]_2$	(Ru-SiMe$_3$)	2-21
Ru-Ge	2.481(1)	*trans*-$Ru(GeCl_3)_2(CO)_4$		2-18
	2.487(5)	*cis*-$Ru(GeCl_3)_2(CO)_4$		2-18
Ru-Ru	2.629(2)	$[Ru(PPh_2XPPh_3)(NO)]_2$		2-142
	2.632(2)	$Ru_2Cl_2(CO)_4(PBu^t_2C_6H_4Me\text{-}p)_2$		2-24
	2.728(2)-2.749(2)	$(C_8H_{10})Ru_4(CO)_{11}$		2-34
	2.764(7)-2.818(7)	$H_2Ru_4(CO)_{13}$		1-12
	2.775(5)-2.811(8)	$(C_{12}H_{16})Ru_4(CO)_{10}$		2-35
	2.783(5)	$HRu_3(CO)_9(C_6H_9)$		1-16
	2.787(2)	$[RuCl(PPh_2)(NO)]_4$		2-142
	2.823(2)	$(C_8H_{10})Ru_4(CO)_{11}$	('hinge')	2-34
	2.850(6)	$(C_{12}H_{16})Ru_4(CO)_{10}$	('hinge')	2-35

	2.861, 2.870(1)	$Ru_3(CO)_{10}(NO)_2$		1-13
	2.889(6)	$HRu_2[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$		2-58
	2.915(7)-2.947(6)	$H_2Ru_4(CO)_{13}$	(H-bridged)	1-12
	2.958(3)	$[Ru(SiMe_3)(SiMe_2)(CO)_3]_2$		2-21
	2.964(6)	$HRu_3(CO)_9(C_6H_9)$	(H-bridged)	1-16
Os-Os	2.715, 2.881, 2.960	$HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$		1-15
	2.739, 2.892, 2.918	$HOs_3(CO)_7(PPh_3)(PPh_2)(C_6H_4)$		1-15
	2.747, 2.874, 2.944	$Os_3(CO)_8(C_4Ph_4)$		1-17
	2.757-2.857	$Os_3(CO)_8(C_2Ph_2)_2$		2-36
	2.762, 2.866, 3.001	$HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$		1-15
	2.796, 2.797, 2.985	$Os_3(CO)_7(PPh_2)_2(C_6H_4)$		1-14
	2.863, 2.896, 3.047	$Os_3(CO)_7(PPh_2)_2(C_6H_4)$		1-14
	3.095, 3.107, 3.146	$Os_3(CO)_8(PPh_2)(PPhC_6H_4)(Ph)$		1-14
Co-Hg	2.504(9)	$(\pi-C_5H_5)Co(CO)_2\cdot 3HgCl_2$		2-95
	2.578(4)	$(\pi-C_5H_5)Co(CO)_2\cdot HgCl_2$		2-94
Co-C	1.87(2)-1.90(1)	$PhCCo_3(CO)_6(C_6H_3Me_3)$		2-37
	1.895(7)-1.907(7)	$MeCCo_3(CO)_7(f_4fars)$		1-11
	1.96(1) (av.)	$[CCo_3(CO)_9]_2$		1-10
Co-Ge	2.341(9)	$[(\pi-C_5H_5)Co(CO)]_2(GeCl_2)_2Fe(CO)_4$		1-9
Co-Co	2.439(5)	$[(\pi-C_5H_5)Co(CO)]_2(GeCl_2)_2Fe(CO)_4$		1-9
	2.440(1)	$MeCCo_3(CO)_7(f_4fars)$	(ligand-bridged)	1-11
	2.441(2)-2.477(3)	$PhCCo_3(CO)_6(C_6H_3Me_3)$		2-37
	2.450(9)	$Co_4(CO)_9(f_4fars)_2$		2-133
	2.452(2)	$[(\pi-C_5H_5)Co]_3(CO)(S)$		2-38
	2.457(1)(av.)	$[CCo_3(CO)_9]_2$		1-10
	2.459(6)	$Co_2(CO)_4(HC_2CF_3)_3$		2-70
	2.470(2)-2.479(2)	$MeCCo_3(CO)_7(f_4fars)$		1-11

	2.474(2)	$\{[(\pi\text{-}C_5H_5)Co]_3(S)_2\}^+$		2-38
	2.531(1)	$(C_7H_8)Co_2(CO)_6$		2-62
	2.559(3)	$(C_6H_8)_2Co_2(CO)_4$		2-63
	2.649(1)	$\{[(\pi\text{-}C_5H_5)Co]_3(S)_2\}^+$		2-38
	2.687(3)	$[(\pi\text{-}C_5H_5)Co]_3(S)_2$		2-38
	2.794(2)	$Ba_3[Co_2(CN)_{10}].13H_2O$		2-27
	2.798(2)	$Ba_3[Co_2(CN)_{10}].13H_2O$		2-26
Rh-Rh	2.630(2)	$[Rh(CO)(PPh_3)_2]_2$		1-121
	2.741(2)	$[Rh(PF_3)_2(PPh_3)_2](C_2Ph_2)$		2-71
Ir-Ir	2.554(1)	$[Ir(CO)(PPh_2)(PPh_3)_2]_2$		2-130
Ir-Cu	2.775(4)-2.959(4)	$Ir_2Cu_4(PPh_3)_2(C_2Ph)_8$		2-33
Pd-Pd	2.686(7)	$Pd_2I(C_3H_5)(PPh_3)_2$		1-61
Pt-Pt	2.633(1)	$FePt_2(CO)_5[P(OPh)_3]_3$		1-23
	2.944(2)	$Pt_4(OAc)_6(NO)_2$		2-144
Cu-Cu	2.377, 2.389(3)	$[Me_2NCH_2C_6H_3MeCu]_4$		1-33
	2.48	$[Cu(Me_2NC_6H_4)]_4(CuBr)_2$	(aryl-bridged)	1-34
	2.494(6)-2.595(5)	$H_6Cu_6(PPh_3)_6$		2-28
	2.632(6)-2.674(5)	$H_6Cu_6(PPh_3)_6$	(H-bridged)	2-28
	2.64	$[Cu(Me_2NC_6H_4)]_4(CuBr)_2$		1-34
	2.663(6)-2.829(6)	$Ir_2Cu_4(PPh_3)_2(C_2Ph)_8$		2-33
	2.70	$[Cu(Me_2NC_6H_4)]_4(CuBr)_2$	(Br-bridged)	1-34
Au-Au	2.600(2)-2.718(3)	$Au_{11}[P(C_6H_4F)_3]_7I_3$	(central Au)	2-30
	2.836(4)-3.187(3)	$Au_{11}[P(C_4H_4F)_3]_7I_3$	(peripheral Au)	2-30
	2.934(2)-3.093(2)	$\{Au_6[P(p\text{-}tol)_3]_6\}^{2+}$		2-29

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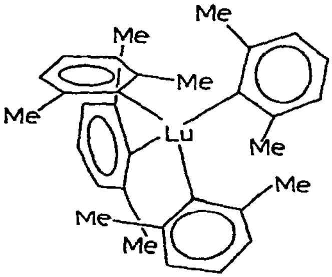
[*] Reference numbers relate to Parts 1 and 2, as denoted by prefix.

(d) Metal-metal bond lengths reported during 1972. Previous surveys contained tabulations of metal-metal bond lengths determined throughout the year surveyed. The Table below lists values reported during 1972 and culled from both Parts of this survey.

COMPLEXES CONTAINING METAL-CARBON σ BONDS

(a) Alkyls, aryls and related compounds. The anion in $[Li(THF)_4][Lu(2,6\text{-}Me_2C_6H_4)]$ (12) consists of the four aryl groups in an approximately tetrahedral array about lutetium.[39] The comple is of interest as the first structurally characterised σ-bonded f-transition metal.

The tris(diethylether)mono(tetrahydrofuran) adduct of Na_2CrPh_5 (13) contains five-coordinate chromium(III), in a distorted trigonal bipyramidal configuration.[40] The sodium ion environment



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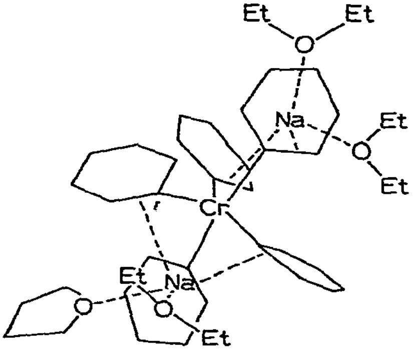

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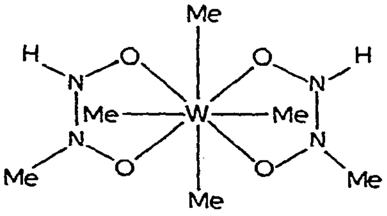

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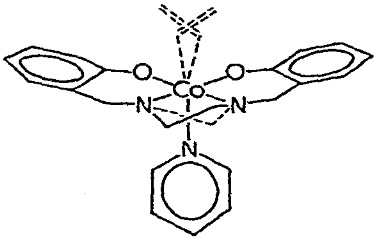

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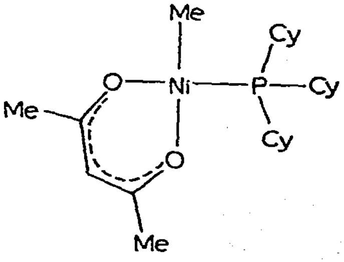


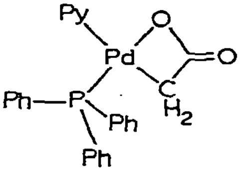
(16)

consists of two phenyl groups, and two oxygen atoms, and Na-C bond distances (2.6-2.8Å) are interpreted on the basis of a trinuclear complex containing Cr-C(Ph)-Na three-centre bonds. The full details of the structure of $[Cr(2\text{-}MeOC_6H_4)_2(bipy)_2]I$ have appeared.[41]

Nitric oxide reacts with WMe_6 affording the eight-coordinate complex (14), containing the N-methyl-N-nitrosohydroxylaminato ligand.[42] In solution, the ^1H N.M.R. spectrum shows that the molecule exhibits non-rigid behaviour.

In complex (15), the axial positions are occupied by vinyl and pyridine ligands, while the salen ligand coordinates using the four equatorial positions of octahedral cobalt.[43] Statistical disorder in the vinyl group and ethylene bridge (in salen) results in an umbrella-shape conformation.

The nickel alkyl $NiMe(acac)(PCy_3)$ (16) contains a Ni-C bond of length 1.94(1)Å.[44] Reactions between keten and $Pd(O_2)(PPh_3)_2$ have given C-bonded chelate derivatives of acetic acid (17) and acetic anhydride (18), characterised by structural studies.[45] The former was studied as the pyridine-PPh_3 complex.



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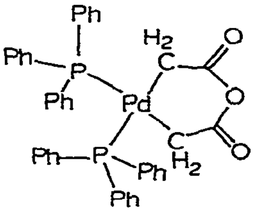

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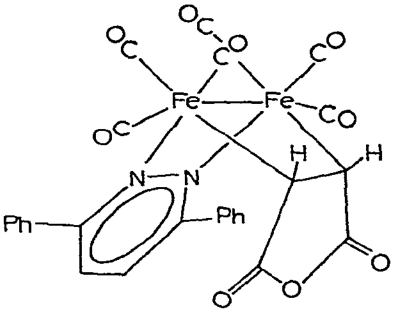
The structure of $Au(C_6F_5)(PPh_3)$ is the expected linear two-coordinate complex,[46] and complements the earlier study of $AuCl(C_6F_5)_2(PPh_3)$.[47] The Au-C bond lengths in the two compounds are 2.07(2) and 2.12-2.18(10)Å, respectively.

The reaction between maleic anhydride and a pyridazine-iron carbonyl complex affords complex (19), by a new type of cycloaddition reaction.[48] This results in the formation of Fe–C σ bonds (to the maleic anhydride fragment). A change in coordination of the pyridazine from a six-electron to a four-electron donor, consistent with some delocalisation within the nitrogen heterocycle, is also found. A similar reaction was found between $[Fe(CO)_3(SCF_3)]_2$ and hexafluorobut-2-yne, giving (20).[49] In this complex, however, a change in donor properties of the sulphur atoms is not possible, and it is the metal-metal bond in the precursor which is involved in the cycloaddition reaction. In the Fe_2S_2 cluster, the orientation of the CF_3 groups is axial,axial.



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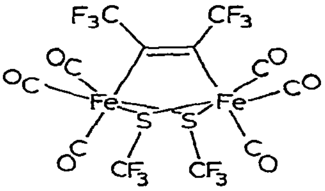

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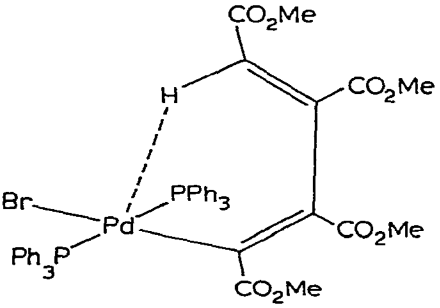

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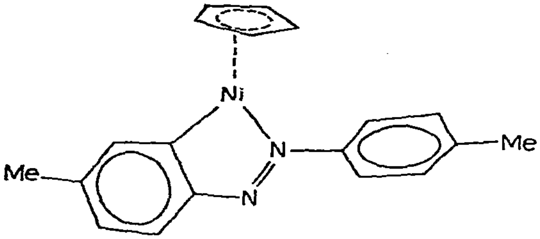
In contrast to the situation in $(\pi\text{-}C_5H_5)Ru(PPh_3)[C_4(CF_3)_4H]$,[50] the butadienyl ligand in trans-$Pd(PPh_3)_2[C_4(CO_2Me)_4H]Br$ (21) is only σ-bonded to the palladium.[51] However, the hydrogen atom occupies a fifth coordination position, with Pd-H (est.) 2.3Å, suggesting some form of bonding interaction. The ^1H n.m.r. data show that this hydrogen resonates at very low field (τ1.40).

Full details of the structure of $[Ir(C_3Ph_3)Cl(CO)(PMe_3)_2]BF_4$ have been reported.[52] This complex contains an IrC_3 metallocycle, being formed by insertion of the metal into the cyclopropenium cation.

(b) Complexes containing internally metallated ligands.

(i) Nitrogen-donor ligands. The geometry of metallated azobenzene and related ligands has been determined. The first complex of this type to be prepared was a cyclopentadienyl nickel derivative; the structure of $(\pi\text{-}C_5H_5)Ni(p\text{-}MeC_6H_3N{:}NC_6H_4Me\text{-}p)$ (22) has been



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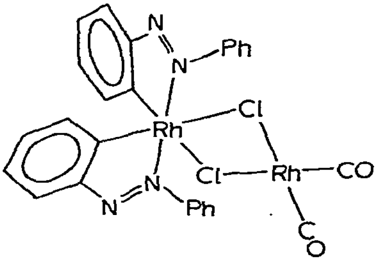

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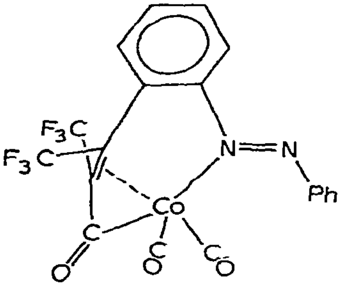
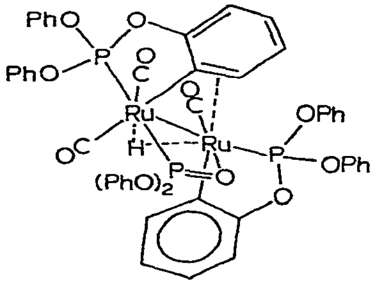


(24)

reported.[53] Complexes containing two ligands bonded to one metal include Rh(OAc)(azb)$_2$, full details of which have now appeared,[54] and the mixed-valence compound (azb)$_2$RhCl$_2$Rh(CO)$_2$ (23), derived from the corresponding chloride.[55] In these examples the two azobenzene ligands are bonded with the nitrogen atoms mutually trans. An intermediate in the reaction between Co(azb)(CO)$_3$ and $C_2(CF_3)_2$ (to give an anilino-quinolone), is the organocobalt complex (24), in which the azoarene is now coordinated via the nitrogen atom adjacent to the substituted ring.[56]

(ii) Phosphorus-donor ligands. Full details of the structure of the complex IrCl$[P(OC_6H_4)(OPh)_2]_2[P(OPh)_3]$ have been published.[57] In the distorted octahedral complex, the two Ir-C bonds are cis, as are the Ir-P bonds to the metallated phosphite ligands. One of the products obtained by controlled pyrolysis of Ru$_3$(CO)$_9[P(OPh)_3]_3$ is the binuclear complex (25), containing a variety of interesting structural features, including (i) a conventionally metallated phosphite ligand (ii) a second such ligand in which the metallated ring also interacts with the second ruthenium atom (iii) a diphenylphosphonate group bridging two metal atoms and (iv) a bridging hydride ligand (not detected in the structural study).[58]



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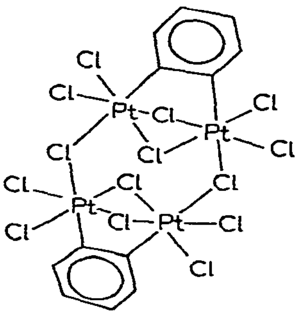


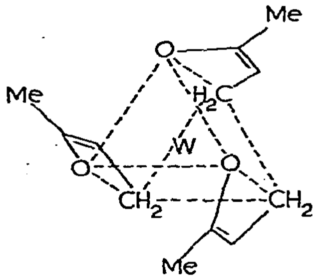
(26)

(iii) Other related compounds. One of the compounds obtained from $[PtCl_4]_4$ and Ph_3CCl in benzene is the triphenylcarbenium salt of the unusual anion $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ (26). Bridging chlorine atoms link two $Pt_2(C_6H_4)Cl_6$ moieties, each containing an o-phenylene ring bridging two platinum atoms.[59]

OLEFIN AND DIENE COMPLEXES

Unusual trigonal prismatic coordination of tungsten is found in tris(methylvinylketone)tungsten (27); bond distances suggest the enone-metal interaction is best represented as the σ-π type shown.[60]

A trans-butadiene ligand bridges the two $Mn(CO)_4$ groups in $(C_4H_6)Mn_2(CO)_8$ (28); all C-C bond distances are equal (1.45Å). Two cobalt complexes containing dienes are $(C_7H_8)Co_2(CO)_6$ (29)[62] and



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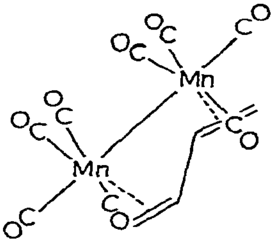

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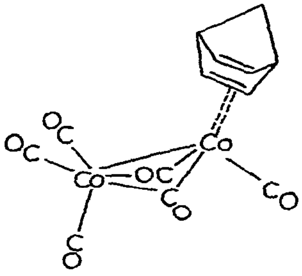

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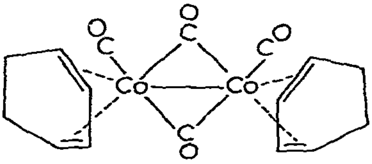
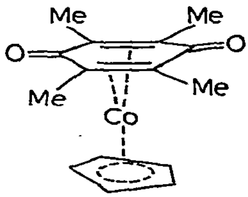


(30)

$[(C_6H_8)Co(CO)_2]_2$ (30).[63] In the former, norbornadiene chelates to one metal atom, which is linked to a $Co(CO)_3$ group via two asymmetrically bridging CO groups and a metal-metal bond. In the cyclohexa-1,3-diene complex, the $Co_2(CO)_4$ moiety has the cis-bridged conformation.

The dihydrate of the duroquinone complex (π-C_5H_5)Co(DQ) has structure (31); this structure is compared with a variety of related molecules, and evidence for a stronger metal-duroquinone interaction than in the isoelectronic (COD)Ni(DQ) is given.[64] The water molecules hydrogen-bond to the quinoid oxygen, and there is also one O-H...O(water) bond.

The fluxional five-coordinate iridium compound $IrMe(COD)(PMe_2Ph)_2$ has structure (32).[65] The iridium has essentially trigonal-bipyramidal coordination, with the two phosphines and one double bond in the equatorial positions.



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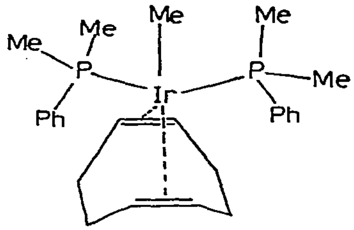

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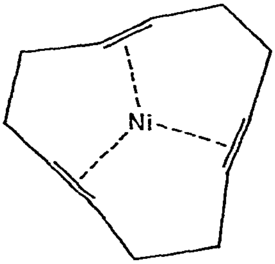

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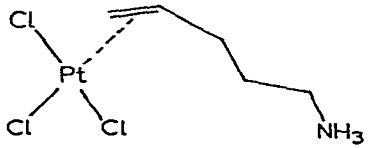
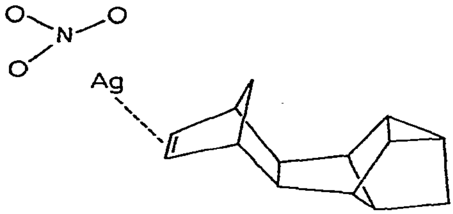


(34)

In $IrCl(CO)(AsPh_3)_2(TCNE)$, the geometry is essentially the same as that found in $IrBr(CO)(PPh_3)_2(TCNE)$, bond length differences being of only marginal significance.[66]

all-trans-Cyclododecatrienenickel has structure (33), with the nickel embedded in the ring and having trigonal coordination.[67] The structure of trichloro(pent-4-enylammonium)platinum (34) is very similar in both the yellow and orange crystalline forms; only the conformation of part of the olefinic chain is different. In the solid state, intermolecular N-H---Cl hydrogen bonds stabilise the structure.[68]



(35)

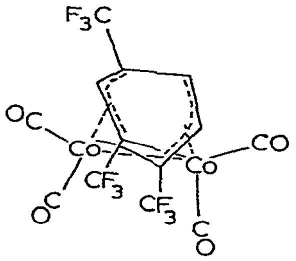
The silver nitrate adduct of one of the isomers of a norbornadiene dimer, produced by the photochemical dimerisation of norbornadiene catalysed by nickel carbonyl, has structure (35)), enabling firm structure assignments to be made for all four Diels-Alder dimers.[69]

COMPLEXES OBTAINED FROM ACETYLENES

The structure of the 'flyover' complex $Co_2(CO)_4(CF_3C_2H)_3$ (36), obtained from $Co_2(CO)_8$ and trifluoropropyne, contains the CF_3 groups attached to the 1,3 and 6 positions of the six-carbon bridge.[70] Bonding of the bridging ligand occurs via a π-allyl and σ-carbon-metal bond to each cobalt. The rhodium derivative $Rh_2(PF_3)_4(PPh_3)_2(C_2Ph_2)$ (37) is similar to $Co_2(CO)_6(C_2Ph_2)$, with the acetylene symmetrically bridging a Rh-Rh bond.[71] This and related complexes are stereochemically non-rigid, the ^{19}F n.m.r. spectra indicating intramolecular exchange of coordinated PF_3 groups.

The intermediate adduct of hexafluorobut-2-yne and <u>trans</u>-$PtClMe(AsMe_3)_2$ has been isolated, and the structure has now been confirmed (38).[72] The alkyne occupies an equatorial position (if the platinum is considered to be 5-coordinate), together with the phosphines. The Pt–Cl bond length [2.47(1)Å] reflects the strong <u>trans</u>-influence of the methyl group. The CF_3 groups are bent away from platinum by 135(4) and 150(4)°.

A symmetrical acetylene-copper π bond is found[73] in the CuCl adduct of $(\pi\text{-}C_5H_5)Fe(CO)_2C_2Ph$; in this compound (39), the acetylene substituents are bent back some 18°. Dimerisation occurs with the formation of Cu–Cl–Cu bridges.



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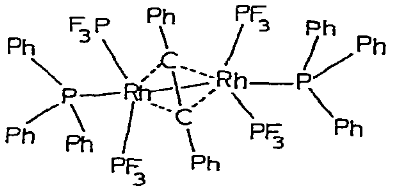

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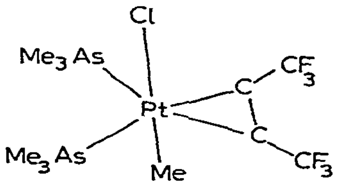

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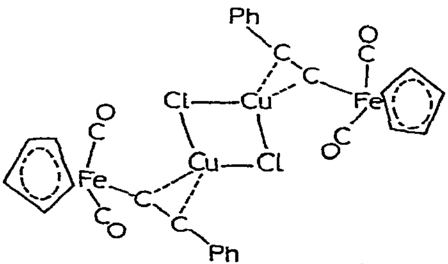

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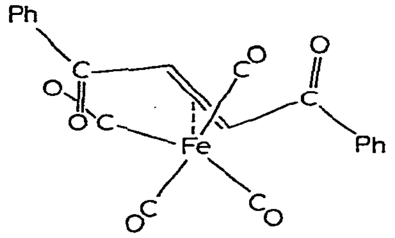
IRON CARBONYL DERIVATIVES OF UNSATURATED LIGANDS

The variety and scope of reactions of iron carbonyls with unsaturated ligands has probably resulted in the isolation of complexes of a wider range of structural types than found for any other element. The period under review has shown no slackening in this respect, and in this Section are collected details of these compounds.

In the simple olefinic complex with trans-1,2-dibenzoylethylene (40),[74] the ethylene occupies an equatorial position; the ligand is



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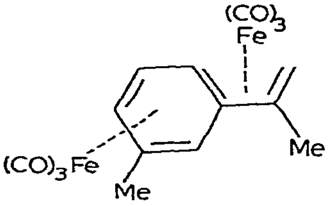

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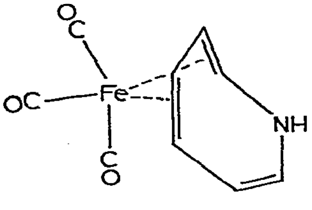

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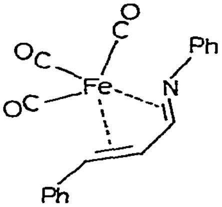

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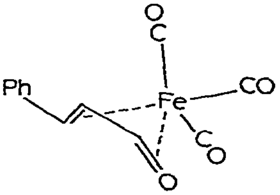

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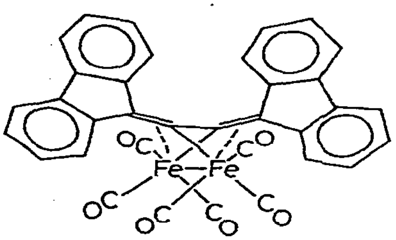


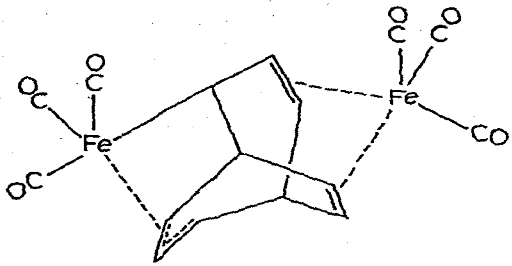
(45)

no longer planar, with a C=C bond length of 1.47Å. A bis-Fe(CO)$_3$ complex of 3,α-dimethylstyrene (41) contains two linked planar isoprene-Fe(CO)$_3$ units, resulting in a trapped Kekulé structure for the aromatic portion of the molecule, with the two metal atoms having a <u>trans</u> configuration.[75] Diene-Fe(CO)$_3$ complexes studied also include azepine-Fe(CO)$_3$ (42), which is reported together with an extensive account of the bonding in this and 23 related molecules.[76]

The structures of both the monoclinic and orthorhombic forms of (N-cinnamylideneaniline)Fe(CO)$_3$ (43) have been determined,[77] the molecular structures being indistinguishable in both forms. The hetero-butadiene fragment is not planar, with the nitrogen being displaced towards the metal atom. The related cinnamaldehyde-Fe(CO)$_3$ complex (44) exhibits a similar feature.[78] However, in both cases, the ligand is π-bonded, the hetero-atom lone pairs playing no part in the bonding.

A butatriene complex contains the ligand attached to two atoms via σ and π bonds (45); an alternative description involves asymmetric bonding to two π-allyl fragments.[79] Unit cell data for three related complexes are included. The binuclear bullvalene derivative, $C_{10}H_{10}Fe_2(CO)_6$ (46), contains one Fe(CO)$_3$ group attached by two π-olefinic bonds, while the other is bonded via a σ bond and a π-allyl group, having opened the C_3 ring in the parent hydrocarbon.[80] A similar insertion into the C_3 ring of dibenzosemibullvalene occurs, but in this case a four-membered C_3Fe metallocycle (ferretane) (47) is formed, as shown by a crystal structure determination.[81]

A further example of a metallocycle is complex (48), obtained from the reaction between diphenyldiazomethane and a dimethoxyferrole complex.[82] As mentioned earlier [AS70; 92], in the formation of this compound some rearrangement of the methoxy group



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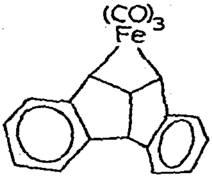

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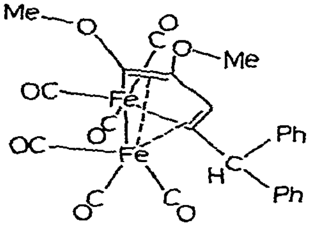


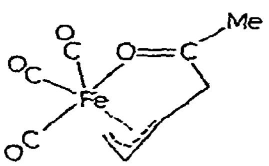
(48)

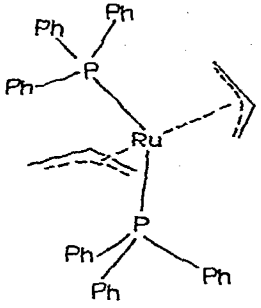
substitutution has occurred, so that these groups are now on adjacent carbon atoms.

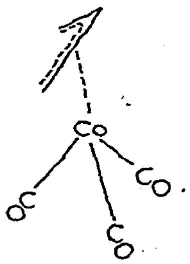
ALLYLIC COMPLEXES

The intermediate in the Friedel-Crafts acetylation of butadiene-Fe$(CO)_3$ is the allylic cation (49), studied as the hexafluorophosphate; in addition to the π-bonded C_3 moiety, the oxygen atom is also involved in bonding to the metal.[83]

There are no significant differences in the appropriate bond lengths in $(\pi\text{-}C_3H_5)_2Ru(PPh_3)_2$ (50) to suggest asymmetric bonding of the allyl groups.[84] The ruthenium coordination is tetrahedral. An electron-diffraction study of $(\pi\text{-}C_3H_5)Co(CO)_3$ (51) has been reported[85]; the angle between the plane of the C_3 group and that of the three carbonyl carbon atoms is 36°.



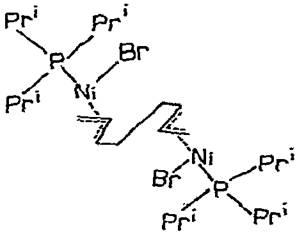


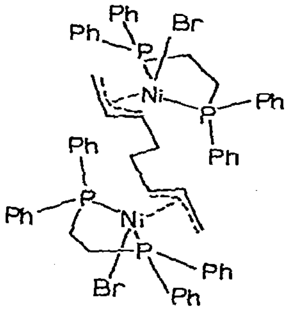


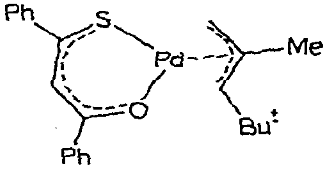
(49) (50) (51)

Dimerisation of butadiene with $NiBrMe(PPr^i_3)_2$ gives the orange intermediate $C_8H_{12}[NiBr(PPr^i_3)]_2$ (52), which on treatment with bis(diphenylphosphino)ethane affords red $C_8H_{12}[NiBr(dppe)]_2$ (53).[86] In (52), the nickel is four-coordinate square planar, while in (53), the metal is five-coordinate square bipyramidal. The latter readily forms the four-coordinate cation $\{C_8H_{12}[Ni(dppe)]_2\}^+$, and the long Ni-Br bond length (2.66Å) suggests partial ionic character for this bond.

In $(Bu^tCHCMeCH_2)Pd(PhCOCHCSPh)$, the *syn*/*trans* structure (54) is found; the *trans* influences of the thio-β-diketone bonding atoms can be judged from the Pd-C distances of 2.18(1)Å (*trans* to S) and 2.05(1)Å (*trans* to O).[87]



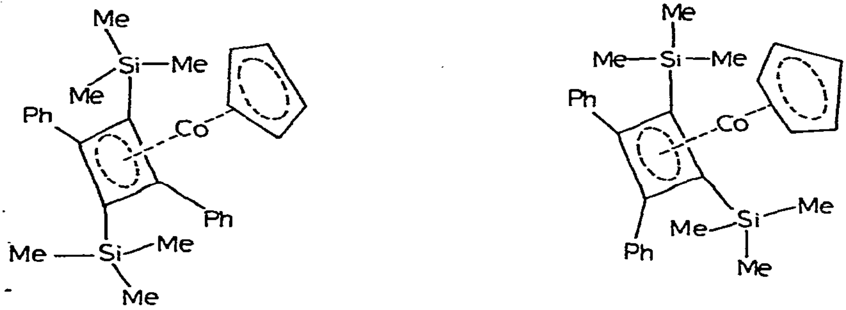




(52) (53) (54)

CYCLOBUTADIENE COMPLEXES

Two independent determinations[88,89] of the structure of the trans isomer of $(\pi\text{-}C_5H_5)Co[\pi\text{-}C_4Ph_2(SiMe_3)_2]$ (55), and one[89] of the cis isomer, have been reported. In both compounds, the ring planes are parallel, and the metal-ring centre distances are the same for both rings. Internal angles in the C_4 ring suggest that whereas the ring is exactly square in the trans isomer, it becomes trapezoid in the cis form.

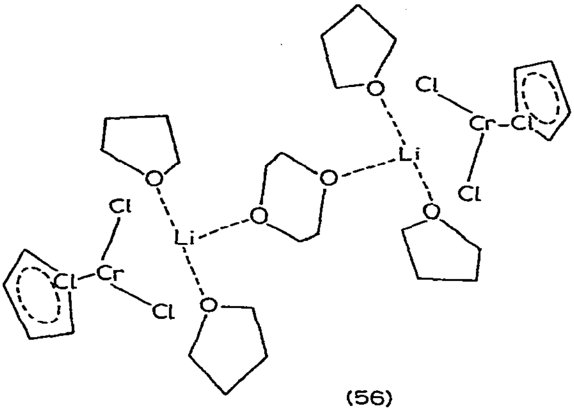


trans (55) *cis*

CYCLOPENTADIENYL COMPLEXES

The structure of $(\pi\text{-}C_5H_5)_2TiCl_2$ has been reported,[90] and is similar to other compounds of this type; some differences in bond parameters were noted in a comparison with the earlier electron diffraction study. Some crystal data for the 1,1'-trimethylene-bridged zirconium and hafnium derivatives have been given.[91]

The dioxan-bridged tetrahydrofuranate of $LiCrCl_3(C_5H_5)$ has structure (56); the Cr-C (cyclopentadienyl) bond lengths range from 2.211(18) to 2.322(18)Å.[92] The interesting complex $[(\pi\text{-}C_5Me_5)Cr(CO)_2]_2$ (57) contains a short, unbridged Cr-Cr bond, intermediate in length between those in $Cr(OAc)_2$ and $Cr_2(C_3H_5)_4$.[93]



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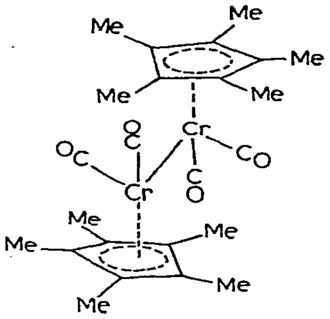
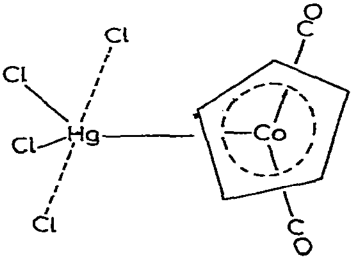


(57)

Full details of the structure of the mercury (II) chloride adduct of $(\pi\text{-}C_5H_5)Co(CO)_2$ (58) have appeared.[94] The complex is a 1:1 Lewis acid-base adduct bonded via the metal atoms. Although formal coordination about mercury is trigonal planar, two long Hg---Cl contacts occur in the axial positions of a trigonal bipyramid. A 3:1 adduct is best formulated[95] as a salt $[(\pi\text{-}C_5H_5)Co(CO)_2(HgCl)]Cl$ (59) containing two additional molecules of $HgCl_2$; the Co-Hg bond is significantly shorter than that found in (58).



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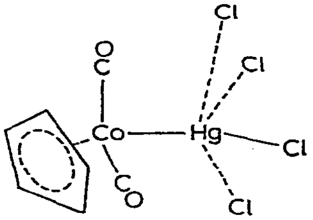


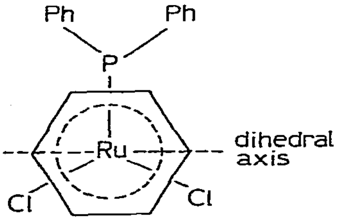
Additional Hg---Cl interactions also down

(59)

COMPLEXES CONTAINING C_6 OR C_8 RINGS

Combined X-ray and neutron diffraction results on $(\pi\text{-}C_6H_6)Cr(CO)_3$ at 78K have been obtained.[96] Compared to benzene, three of the benzene C-C bonds (those directly over the Cr-CO bonds) are lengthened by 0.018(2)Å, the others being unaffected. Although this distortion is small, both diffraction studies show it, and it is outside experimental error. The authors point out that if bonding from the metal to the ring occurs preferentially to the longer bonds, then the chromium has trigonal-prismatic coordination.

Brief details of $(C_6H_6)RuCl_2(PMePh_2)$ (60) and the *p*-cymene complex reveal distorted *hexahapto* arene ligands, probably as a result of the *trans* bond-weaking effect of the phosphine ligand.[97] The rings are bent, with a dihedral of 5° (benzene) and 2° (*p*-cymene), suggesting significant localisation of the ring π electrons. A bent (43°) C_6-ring is also found in $Ru(C_6Me_6)_2$ (61), although in this example it bonds as a *tetrahapto* ligand.[98] In contrast to the C_6-Ru-C_4 arrangement in (61), the bonding in a bis(cyclohexadienyl)iron complex (62) is of the C_5-Fe-C_5 type, the orientations of the two π-pentadienyl systems minimising steric interactions while maximising the number of eclipsed π bonds, i.e. a centrosymmetric conformation is *not* assumed.[99] Unit cell data for four (π-arene)iron(π-cyclopentadienyl)-cations have been listed recently.[100]



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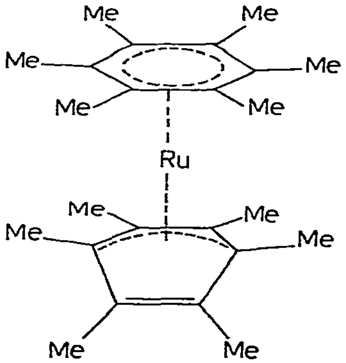

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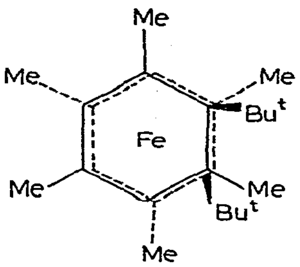

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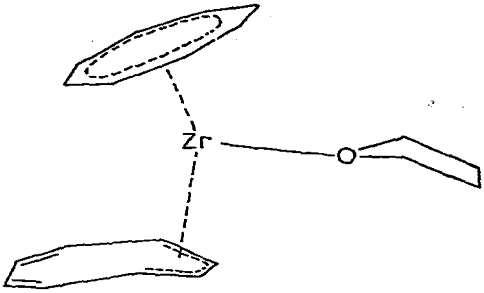
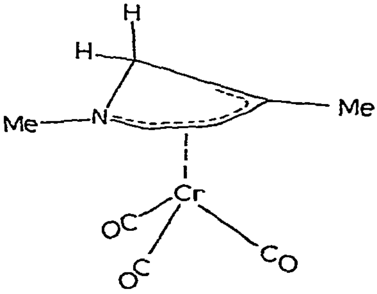


(63)

A further example of a cyclooctatetraene complex, $Zr(C_8H_8)_2(THF)$ (63), contains one C_8 ring bonded via all eight carbons, while the second forms a tetrahapto attachment.[101] In the latter, the "butadiene" fragment is somewhat distorted. The tetrahydrofuran is only weakly coordinated, being readily displaced, and this observation is in accord with the very long Zr–O bond [2.447(4)Å].

Π-BONDED HETEROCYCLIC SYSTEMS

Full details of the structures of $Co(C_5H_5BR)_2$ (R = Me or OMe) have appeared.[102] Both molecules are centrosymmetric, the rings being nearly planar, and bond distances indicating a degree of cyclic conjugation. The boron atoms are as far as possible from one another.

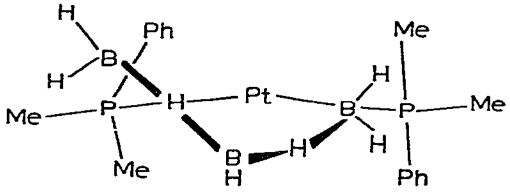


(64)

A further description[103] of the structure of $(Et_6B_3N_3)Cr(CO)_3$ shows the slight distortion of the ring towards the chair conformation. The nitrogen atoms and carbonyl groups are staggered. In the dihydropyridine complex (64), the chromium is bonded to five atoms of the heterocycle, with the methylene group bent away from the metal.[104]

COMPLEXES CONTAINING OTHER DONOR ATOM LIGANDS

(a) Boron Ligands Structural parameters have been determined for the π-borallyl ligand in $Pt(\pi\text{-}B_3H_7)(PMe_2Ph)_2$ (65).[105] The dihedral angle between the B_3 plane and the PtP_2 plane is 116.8(24)°. The boron ligand is asymmetrically bonded to platinum, and is orientationally disordered; the hydrogen atoms were not located. The anion $[Ni(B_{10}H_{12})_2]^{2-}$ (66) contains the nickel attached to two B_4 faces fusing two 11-atom polyhedra containing open pentagonal faces.[106]



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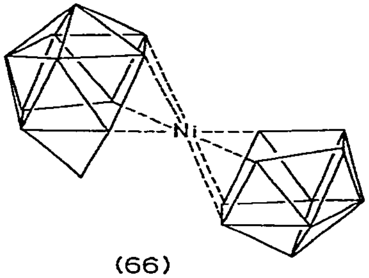
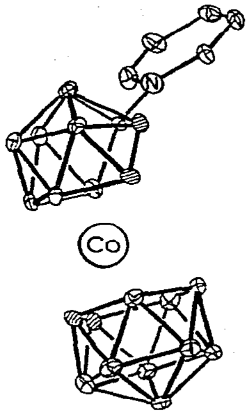


(66)

Base degradation of $\{Co[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2\}^-$, followed by oxidation and treatment with pyridine, affords $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)]^-$, isolated as the NEt_4 salt (67). The $(B_8C_2H_{10}py)^{2-}$ ligand contains a B_8C_2 framework defining an icosahedron from which two mutually ortho apices have been removed, coordination to cobalt being via a B_3C face.[107] The carborane ligand in $(\pi\text{-}C_5H_5)Co(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$ (68) forms, with the cobalt atom, a triangulated (1,5,6,1) 13-apex decosahedron, the



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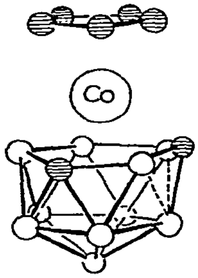
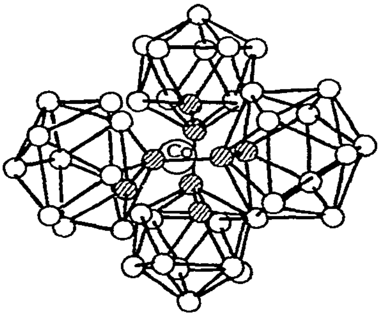


(68)

metal being bonded to a B_3CBC face.[108] The biscarborane complex NEt_4-$\{Co[(B_{10}C_2H_{10})_2]_2\}$ (69) contains four carborane icosahedra tetrahedrally arranged about cobalt.[109] This does not result in a tetrahedral coordination of four bonding carbon atoms; the environment of the metal atom is a distorted square pyramid, the basal plane being defined by three carbons and one hydrogen (as part of a B-H-Co bridge) (69a).

(b) Carbenes and isonitriles The *cis* and *trans* isomers of $PtCl_2[C(NPhCH_2)_2](PEt_3)$ have been compared[110]; using the Pt-Cl bond



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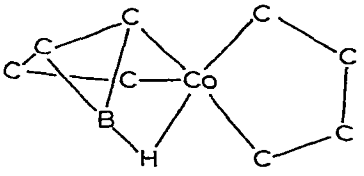
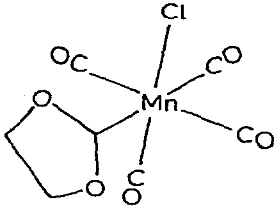


(69a) Environment of the cobalt atom in (69) lengths as the criterion, the trans influence of this carbene is greater than that of π-acids (e.g. CO, isonitriles), but less than that of σ-vinyl. The molecular structure of cis-$MnCl(COCH_2CH_2O)(CO)_4$ (70) has been reported[111]; the Mn-C (carbene) bond length is 1.96(1)Å.

In the dimethylimidazolinylidene-iron complex (71) an axial carbonyl group has been substituted by the carbene ligand, the stereochemistry being considerably distorted from ideal trigonal



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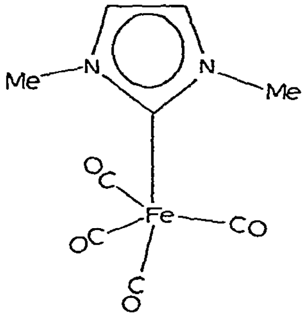

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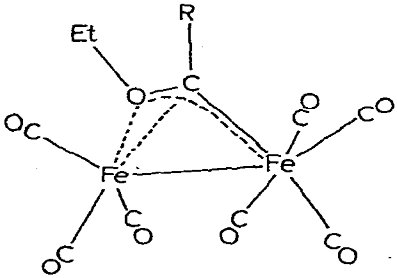
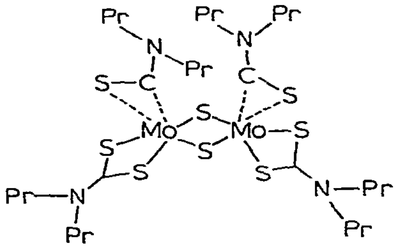


(72) R = 2,6-$(MeO)_2C_6H_3$

bipyramidal.[112] The binuclear compound (72) contains an $Fe(CO)_3$ group bonded to the carbene ligand in a substituted-phenyl(ethoxy)carbene-$Fe(CO)_4$ complex.[113] Some similarities to the structure of the $Fe(CO)_3$ adduct of a β-acetylvinyliron complex are apparent.[114]

An unusual carbene complex is formed from molybdenum(II) acetate and dialkyldithiocarbamate by C–S bond cleavage.[115] The complex $[Mo(SCNPr_2)(S_2CNPr_2)]_2S_2$ has structure (73). Although the thiocarbomoyl-Mo bond is similar to the CS-Pt bond in $Pt(CS_2)(PPh_3)_2$, the Mo–C bond length [2.066(8)Å] indicates a bond order of ∼1.5, and is close to that found in the chelate carbene $(\pi\text{-}C_5H_5)(CO)_2MoNHNC(CO_2Et)COH$.



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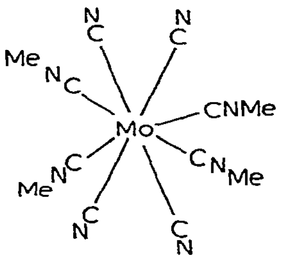
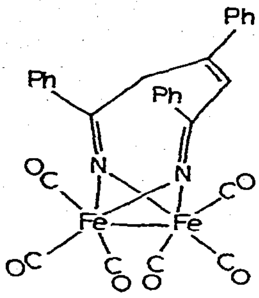


(74)

The eight-coordinate complex $Mo(CN)_4(CNMe)_4$ has structure (74), in which the molecule adopts the dodecahedral configuration with cyanide groups in the A positions, and isonitrile groups in the B positions.[116]

(c) Nitrogen-donor ligands The results of structural studies of diazepine complexes containing iron and rhodium carbonyl moieties have been discussed.[117] In the former, the heterocycle opens to form a diiminato-$Fe_2(CO)_6$ complex (75), whereas with rhodium, the unchanged ligand is attached by only one nitrogen.

From meso-tetraphenylphorphin (ms-TPP) and $Re_2(CO)_{10}$, the binuclear complex (ms-TPP)$Re_2(CO)_6$ can be prepared, and has been shown to contain the structural unit (76).[118] The two metal atoms are attached to one porphin ligand, above and below the plane, and offset so that each metal is bonded to three nitrogen atoms. The Re–Re



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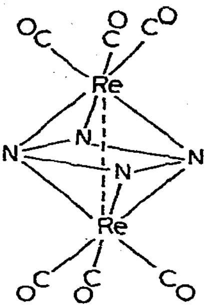
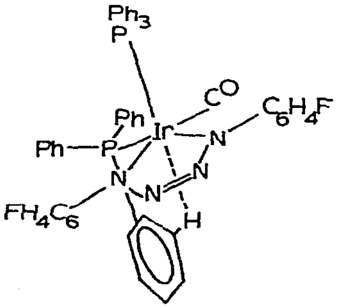


(76) Only nitrogens of porpl ligand shown

distance [3.126(3)Å] is outside the usual range of Re-Re bonds (2.7-3.02Å), and a conventional electron count does not require such a bond. However, some type of metal-metal interaction cannot be ruled out entirely.

One of the compounds obtained from reactions between Vaska's complex and p-$FC_6H_4N_2^+BF_4^-$ is the cationic tetrazene-iridium complex (77). The cation is five-coordinate, and contains a planar IrN_4 ring; full details of this structure are now available.[119] The potential sixth position (for distorted octahedral coordination) is blocked by an ortho-hydrogen of one of the PPh_3 ligands (Ir---H, 2.9Å).



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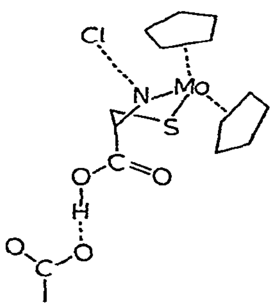

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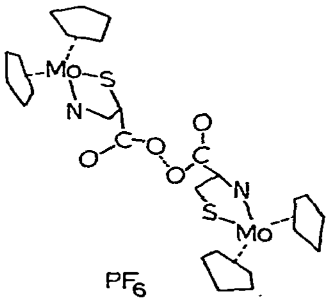
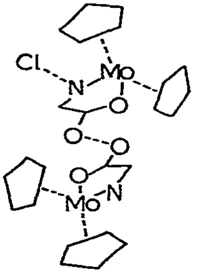


(79)

The structures of four bis(π-cyclopentadienyl)molybdenum derivatives of amino acids have been determined.[120] The L-cysteine complex, studied as the chloride (78) and the hexafluorophosphate (79), contains a hydrogen-bonded dimer (via the carboxylate groups); the amino acid chelates molybdenum via nitrogen and sulphur, and has different conformations in the two salts. The molybdenum is chelated through oxygen and nitrogen in the glycine (80) and sarcosine (81) derivatives. The tungsten tetracarbonyl complex from $N_4P_4(NMe_2)_8$ contains the ligand unusually bonded via a ring nitrogen and an exocyclic NMe_2 group (82).[121]

(d) Phosphorus and arsenic ligands The structure of $MoBr_2(CO)_3$(dppe) (83) confirms the presence of seven-coordinate molybdenum with a slightly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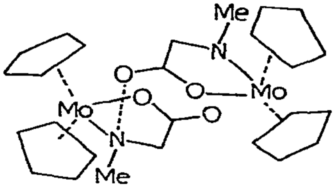
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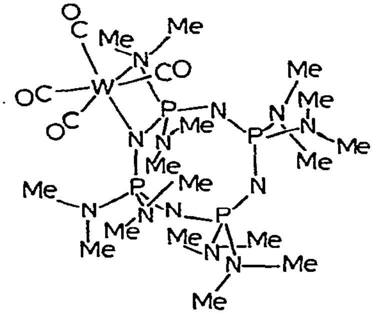
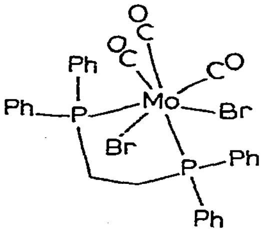

(82)

distorted capped octahedral geometry.[122] Comparisons of metal-phosphorus bond lengths in analogous phosphine and phosphite complexes are rare; in *trans*-$(\pi\text{-}C_5H_4R)Mo(CO)_2[P(OMe)_3]I$ (R = H or Me)[123] the Mo-P distances are shorter [2.406(9) and 2.388(8)Å, respectively] than in *trans*-$(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$ [2.481(5)Å][124] although the Mo-I distances are essentially constant. Unit cell data for $(CO)_4M(PMe_2)_2M'(CO)_4$ (M = Cr, M' = Cr, W; M = M' = W) have been given.[125] The structure of isomer A of $Br(CO)_3Mn(triphos)Cr(CO)_5$ (84) reveals the ligand acting as bidentate towards manganese, and monodentate towards chromium.[126]



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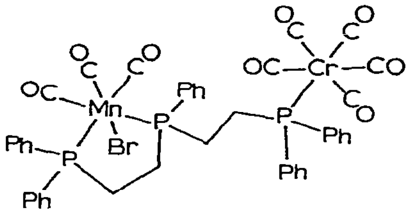
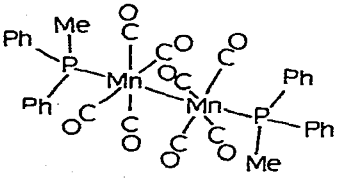


(84)

In $Mn_2(CO)_8(PMePh_2)_2$ (85), the phosphine ligands substitute axial CO groups, whereas in $Mn_2(CO)_8(AsMe_2Ph)_2$ (86), the arsine ligands are equatorial. This distinction is ascribed[127] to differences



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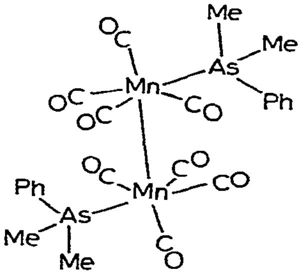
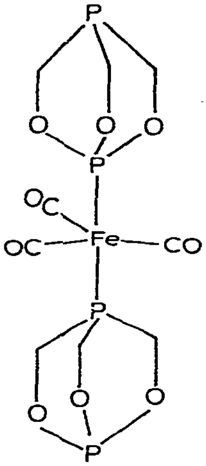


(86)

in Mn-E and E-C bond lengths (E = P or As), allowing statistically favoured equatorial substitution to occur when these bonds are longer, i.e. when E = As.

The structure of trans-Fe(CO)$_3$[P(OCH$_2$)$_3$P]$_2$ (87) has been reported[128]; the complex contains one ligand bonded via the P(CH$_2$)$_3$ group, i.e. as a phosphine, and the other via the PO$_3$ group, i.e. as a phosphite. The two Fe-P bond distances are 2.190(4) and 2.116(4)Å, respectively.



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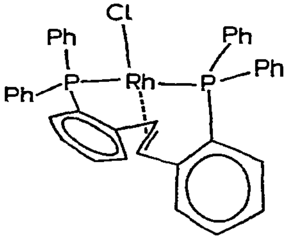

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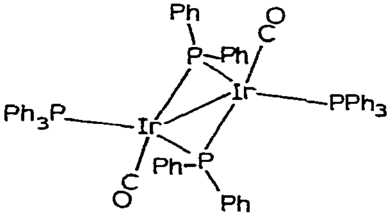
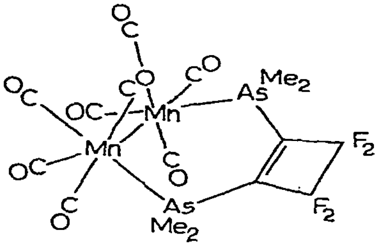


(88a)

Dehydrogenation of 2,2'-bis(diphenylphosphino)bibenzyl in the presence of rhodium(I) or (III) complexes affords the chelate olefin complex (88).[129] Controlled pyrolysis of $IrH(CO)(PPh_3)_2$ in refluxing decalin affords the binuclear phosphido complex (88a), containing an Ir–Ir bond of order two.[130]



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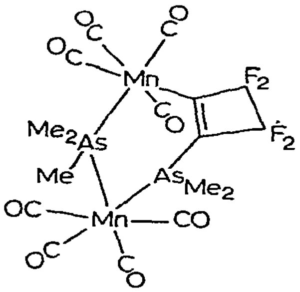
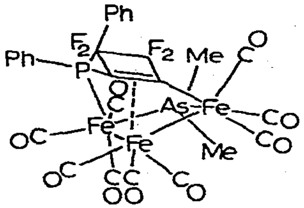
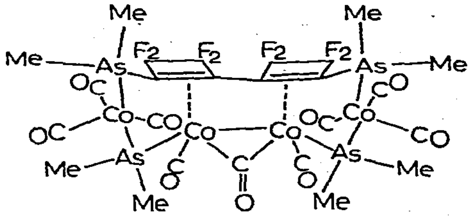


(90)

The range of complexes obtained from fluorocarbon-bridged bidentate phosphine and arsine ligands by Cullen and coworkers continues to expand, and has provided several more unusual complexes during the period under review. Two products obtained from $f_4$fars and $Mn_2(CO)_{10}$ have structures (89) and (90).[131] In the latter, isomerisation of the ligand by cleavage of an As–C bond has occurred, to give a complex containing a bridging $AsMe_2$ group, and an Mn–C σ bond. Using the mixed P,As-donor ligand $f_4$asp, $Fe_3(CO)_{12}$ affords the complex $(f_4asp)Fe_3(CO)_9$, shown[132] to have structure (91), in which a similar cleavage of the $AsMe_2$ group has occurred, with formation of a four-atom $AsFe_3$ cluster. Heating $Co_2(CO)_6(f_4fars)$ also causes cleavage of an $AsMe_2$ group; dimerisation of the cylcobutenyl residues occurs, the resulting complex having structure (92).[133] The complex also contains two hydride ligands (not shown).

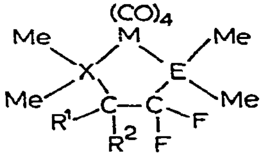


(91)



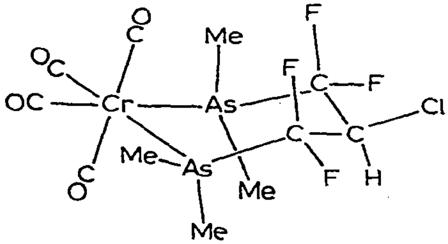
(92)

As mentioned in a previous report [AS71; 338], some structures of complexes (93) have been found[134] to contain disordered arrangements of molecules with normal geometries and dimensions. At each lattice site, two molecular configurations are distributed in occupancy ratios varying from 1:1 to 6:1. These complexes contain five-membered chelate rings which have the usual puckered conformation. Fluorine atoms occupy axial positions. The structure of the related complex $(Me_2AsCF_2CHClCF_2AsMe_2)Cr(CO)_4$ (94) has also been studied[135] as an example of a complex containing a six-membered chelate ring. This ring has the chair conformation, with chlorine occupying a less sterically hindered equatorial position.



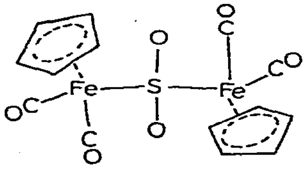
(93)

M	E	R¹	R²
Cr	As	H	H
Cr	As	F	H
Cr	As	F	Cl
Mo	P	F	H
Mo	As	F	H
Mo	As	F	CF$_3$

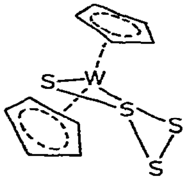


(94)

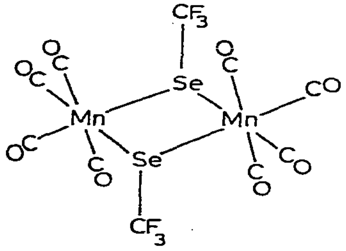
(e) Sulphur and selenium ligands The first complex in which SO_2 alone bridges two transition metals is $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SO_2$ (95); the sulphur is directly attached to the two iron atoms and has a distorted tetrahedral stereochemistry.[136] The WS_4 ring in $(\pi\text{-}C_5H_5)_2WS_4$ (96) has two outer S-S bonds of 2.10(5)Å, and a shorter central S-S bond [2.01(6)Å].[137] Structural data for the planar Mn_2Se_2 unit in $[(CF_3Se)Mn(CO)_4]_2$ (97) have been reported[138]; the Mn-Se bonds have a mean length of 2.50Å.



(95)



(96)

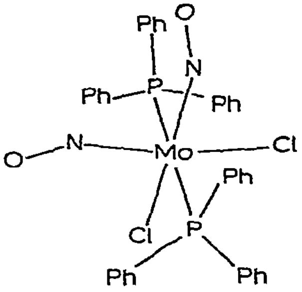


(97)

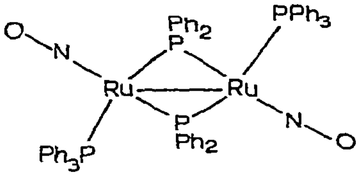
NITROSYLS AND DINITROGEN COMPLEXES

For $Mo(NO)_2Cl_2(PPh_3)_2$ (98), the X-ray diffraction study confirms the cis stereochemistry.[139] Disorder results in half-occupancy of one Cl and one NO site. The Mo-N-O groups are non-linear (angle Mo-N-O, 161.8°), but not sufficiently so to be considered as Lewis acids.

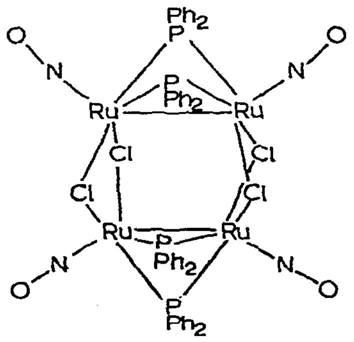
Several ruthenium nitrosyls have been examined, including two studies of the anion $[RuCl_5(NO)]^{2-}$ as the potassium[140] and ammonium[141] salts. In the fomer case, the space group was reassigned. In both, the Ru-Cl bond <u>trans</u> to NO is shorter than the <u>cis</u> Ru-Cl bonds (2.358 <u>vs</u> 2.372Å, respectively). The Ru-N-O group is approximately linear. The reaction between $RuCl_3(NO)(PMePh_2)_2$ and $PHPh_2$ has afforded several products, among which (99) and (100) were characterised by X-ray diffraction methods.[142] The first is a centrosymmetric binuclear complex, related to $[Ir(CO)(PPh_2)(PPh_3)]_2$ (p. 000). Complex (100) is tetranuclear and contains two Ru_2 systems (bridged by diphenylphosphido groups) joined by bridging chlorine atoms. The Ru-N-O angles are 174.1(9)° in (99), and 160.3(8)° in (100).



(98)



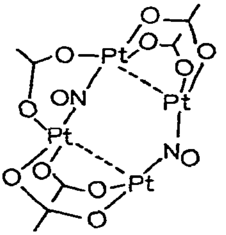
(99)



(100)

The structure of $Ir(NO)(CO)(PPh_3)_2$ has been determined.[143] The iridium has a distorted tetrahedral coordination, with a nearly linear Ir-N-O group. Comparisons of structural parameters of a number of isoelectronic four-coordinate tetrahedral complexes are made.

A product from the preparation of diacetatoplatinum(II) in a reaction involving reduction of Pt^{IV} in HNO_3-HOAc has been shown[144] to be the nitrosyl complex $Pt_4(OAc)_6(NO)_2$ (101), containing bridging nitrosyl and acetato groups. The shorter Pt-Pt separation probably involves some metal-metal interaction.



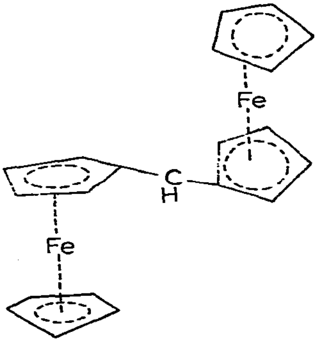
(101)

The complex $[Os(NH_3)_5(N_2)]Cl_2$ contains an octahedral cation with the Os, three NH_3, and the N_2 groups lying on a crystallographic mirror plane.[145] The N-N bond length [1.12(2)Å] is similar to those found in related structures (cf. Table 4, AS71, 340), while the short $Os-N_2$ bond [1.84(1)Å] is indicative of multiple bonding, with a bond order between one and two. Mixtures of $[Ru(NH_3)_5(N_2)]Cl_2$ and $[Ru(NH_3)_5Cl]Cl_2$ form solid solutions isomorphous with the osmium-dinitrogen complex.

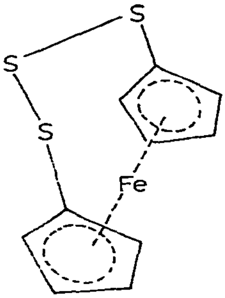
FERROCENE AND BENCHROTRENE DERIVATIVES

A further contribution to the discussion about the stabilisation of metallocene carbonium ions has been the determination of the structure of the α,α-diferrocenylmethylium ion (102)[146]. Although the exocyclic carbon atom does not lie in the planes of either of the two cyclopentadienyl rings to which it is attached, bond distances are not indicative of any strong direct interaction with the metal atom. In the fluxional molecule 1,2,3-trithia[3]ferrocenophane (103), the rings are nearly eclipsed (angle of twist, 0.08°), and are canted towards each other with an angle of 2.85°.[147]

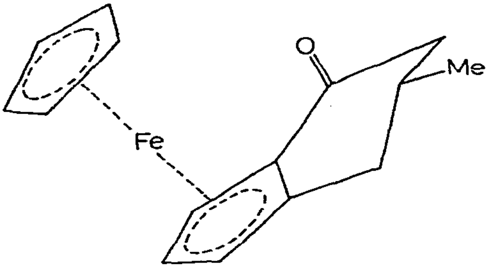
The levorotatory isomer of the ferrocenocyclohexenone m.p. 110°, $[\alpha]_D^{25°}$ −580° ($CHCl_3$, c 1), has structure (104).[148] The absolute configuration of the isomer of (+)-o-methoxy(1'-hydroxyethyl)-benchrotrene (105), m.p. 70°, has also been determined.[149]



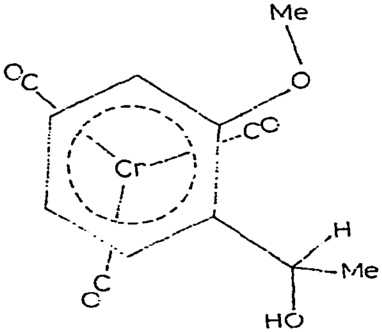
(102)



(103)



(104)



(105)

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